Nanoparticles applied to stone buildings

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Stone has been widely used as a construction material since ancient times, and its preservation is crucial in historical and contemporary buildings. Biodeterioration and other alterations cause damage in stone monuments which leads to the need for repeated actions. Nanotechnology is increasing the development of new products for construction and restoration, and new treatments based on nanoparticles have been developed for stone conservation, such as biocides or consolidants. These treatments avoid the disadvantages of traditional products, such as limewater for consolidation or quaternary ammonium salts as biocide and fulfil some of the requirements demanded by cultural heritage, i.e., effectiveness, compatibility with the stone and its aesthetic values and durability. This manuscript reviews some of the main advances in the development and application of nanoparticles as consolidants and biocides to treat stone cultural heritage.

Keywords: stone, nanoparticles, consolidant, biocide, conservation

1. Introduction

From the origins of mankind, men have used stone as construction material, from Neolithic buildings to colossal constructions like pyramids or gothic cathedrals. In all these cases, both civil and religious works, stone is used, rather than other materials such as wood or clay, because of its high strength. The durability of stone as construction and decoration material is defined as its capacity to withstand decay keeping its mechanical properties as well as its aesthetic qualities, and it is highly influenced by the own characteristics of the material (composition, porosity, texture …) and by its environment (temperature, humidity, wind, atmospheric pollution, etc.) (Benavente, Bernabéu, and Cañaveras 2004). Experience has shown that even a material as durable as stone suffers from slow degradation due both to its intrinsic properties as well as to extrinsic factors. In this sense, its degradation process has been accelerated in the last decades due to anthropogenic factors. The industrialization process has led to an increase in environmental pollution and, consequently, to a series of alterations such as black crusts, which accelerate the degradation of the stone used in the vernacular and monumental architecture located near the emission points (Grossi and Brimblecombe 2007; R. Ortiz et al. 2012).

The implantation of science at all stages of an intervention, and not only at the diagnostic stage, has favoured the introduction of new materials and products for the restoration of stone during the twentieth century. However, initially, these new products were just the adaptation of products used in other sectors, like for instance the chemical industry. Despite the initial expectations for these materials, over time it has been found that their effects on the stone have not always been the desired ones. This led to a change in trends for the requirements demanded for the products used in restoration and which have been developed in different international regulations such as the Restoration Charters.

Finally, the development of new products and materials, specifically designed for this field of activity, has been enriched by nanotechnological contributions, which are focused especially on the design of new nanomaterials as consolidating agents, water repellents, biocides as well as self-cleaning surfaces.

1.1. The stone as construction material

The types of stone used in the construction of masonries dealing with historical heritage are varied, being usually related to the quarries nearby or to the physical, plastic and aesthetic qualities required in the creative process. Among the different and most widely used stones are limestones, marbles, sandstones and granites (Calvo and Regueiro 2010; Galetti, Lazzarini, and Magetti 1992).

The physic-mechanical properties of each type of stone lead themselves to different uses and to be chosen as building material (quarried stones) or as decoration (ornamental stones), as well as its state of conservation and durability. Among the properties of the stone that concern their durability, we must highlight their chemical and mineralogical composition, their texture, pore size and type, porosity, roughness, permeability and capillarity, as well as their mechanical properties (pressure, compressive, flexion and impact resistance).

1.2. Alteration processes in stones

The stone alteration is a natural process of its ageing as a building material and it is heightened by both intrinsic and extrinsic factors. Among the intrinsic factors we must highlight the chemical and mineralogical composition, and the structure and texture of the rock material. Whereas the extrinsic factors deal with the context where the stone is, such as the presence of water in its different stages (gas, liquid and solid), temperature and temperature fluctuations, atmospheric pollution, wind and particles in suspension, the presence of organisms or biodeterioration, the anthropic factor because of its misuse, inappropriate interventions, etc. The effect of each of these factors either individually or together, is seen in a series of indicators of alteration whose manifestation on the stone is diverse and complex.

The degree of vulnerability of both vernacular and monumental constructions, considered as their state of preservation, is a main factor to guarantee their durability. Knowing the main causes of degradation of the stone walls, allows an approximation of what kind of treatments are needed in the restoration processes. For this purpose, Ortiz and Ortiz (Rocío Ortiz and Ortiz 2016) propose to make an approach to the state of conservation of the monuments by creating a vulnerability index. This methodology has been applied to monuments from the city of Seville (Spain) concluding that an 80% of the studied historical buildings have alterations related to biodeterioration, 50% present alterations due to erosion and arenization, and 90% present black scabs, which lead to the breaking up of the stony material.

Biodeterioration is defined as the set of damages or undesirable changes caused by the action of biological agents (Figure 1). It is worldwide considered to be the responsible of around 20-30% of the total degradation of the stone buildings (Rossi and De Philippis 2015), being difficult to calculate the cultural costs as well as the economic costs derived from cleaning, repairing and restoration processes (Gaylarde, Ribas Silva, and Warscheid 2003).

Biodeterioration is associated to a wide variety of organisms and microorganisms (Figure 1.C). Specifically the first stages of colonization in the stone are carried out by microalgae and cyanobacteria (Li et al. 2018). Biofilm formation involves the association of different microorganisms embedded in an organic mucilaginous matrix, and whose colour is due to the species present in it, the available nutrients and the stage of aging of the colony (Sterflinger and Piñar 2013). One of the main disadvantages of the development of biofilms is that they favor superior species such as fungi, lichens and mosses, which form the biocrust.

The alteration mechanisms on stone associated with biodeterioration can be of two types: physical or chemical. The physical alteration mechanisms are those that result in the loss of cohesion of the substrate due to the mechanical action of organisms and, in microorganisms, they are usually related to their mode of adhesion to the stony substrate (sheaths, film-forming substances, hyphae, etc.) (Caneva, Nugari, and Salvadori 1991). The chemical alteration mechanisms are those in which a chemical reaction takes place whose result can be the transformation or decomposition of the substrate, and which are associated to the metabolism of the microorganisms, since, on the one hand, they consume substances as nutrients (carbonated sources, salts, ...) and, on the other, they excrete products such as pigments and organic acids (Vaillant Carol, Doménech Carbó, and Valentín Rodrigo 2003). Each type of microorganism is related to alteration mechanisms which lead to a series of specific alterations (Table 1).

Lack of cohesion and disintegration are two of the main damages that can be observed on stone materials (Figure 2). They are due to multiple factors, from the physico-chemical features of the stone to exogenous factors. However, these last ones seem to have a greater incidence, especially if the wall is located outdoors. The indicators of alteration related to these pathologies are multiple, and usually they precede the loss of original material, with the subsequent detriment in their aesthetic and mechanical properties. Table 2 shows the main indicators of the loss of cohesion and material, according to the terminology recommended by ICOMOS (ICOMOS and ISCS 2008).

1.3. Main treatments for stone restoration

Treatments for stone conservation-restoration must meet the following requirements:

- Effectiveness
- Durability
- Penetration, without generating interfaces between the treated and untreated areas.
- Maintain the porosity of the stone to allow its perspiration and water circulation
- Chemical compatibility, avoiding chemical reactions or the formation of layers on the substrate
- Avoid altering the aesthetic aspect, both in its colour and its brightness. Besides, the treatment must maintain its properties over time, without deteriorating due to the effect of external agents

The control of the development of biological agents, as well as the treatments for their prevention and disinfection, have become routine tasks within conservation-restoration projects. However, despite the different methods and products, if the environmental conditions become favourable again, the biological agents might reappear, therefore these methods have a low medium-term effectiveness and require continuous applications, with the subsequent risk for the artwork and the increase in costs.

The main treatments applied to eliminate and/or prevent biodeterioration can be classified into four major groups: mechanical, physical, biological and chemical methods.

The mechanical methods consist in the physical elimination of the organisms using brushes, scalpels, vacuum cleaners, scrapers, etc. These methods have two main disadvantages: the impossibility of removing infestations completely as they are superficially cleaned, and the risk of damaging the substrate when using certain instruments (VV.AA 2008).

The physical methods entail the use of electromagnetic and electric radiations with biocidal action. In the case of stone walls, these methods are complex to use due to their dimensions since, as a general rule, they require special rooms (Nugari and Salvadori 2003) or isolation conditions.

Biological methods are those in which other parasitic or antagonistic species are introduced to eradicate the growth of the identified species (Webster and May 2006). One of its main drawbacks is the lack of control of the introduced populations, which can cause new alterations.

Chemical methods consist in applying one or several chemical substances with a biocide effect. They are the most widely used and depending on the organisms that need to be eliminated, they are classified as bactericides, fungicides, algicides, insecticides and herbicides. These methods, among which we must highlight the use of organometallic compounds (tributyltin and its phenolic derivatives) or quaternary ammonium salts, can have several disadvantages such as their short-term effect, high toxicity for humans and the environment, or chemical incompatibilities according to the type of stone substrate on which they are applied (Nugari and Salvadori 2003; R. Kumar and Kumar 1999).

When the purpose of the treatment deals with cohesion, the restorers use consolidant treatments. They can be divided in three major groups depending on their chemical composition: inorganic, silicate based and polymeric.

Among the inorganic consolidants it is worth highlighting the use of limewater, historically one of the most used material. Its consolidant effect is achieved by the chemical reaction of calcium hydroxide ($Ca(OH)_2$) and atmospheric carbon dioxide (CO_2) which forms calcium carbonate ($CaCO_3$). There are many advantages in the use of limewater as a consolidant product, such as its great chemical compatibility with carbonate stones as well as its great durability (Giovanni Borsoi et al. 2017). Among its disadvantages are its low penetration capacity and its limited effectiveness due to its low solubility in water (Daniele, Taglieri, and Quaresima 2008). Another widely used inorganic consolidant is barium hydroxide ($Ba(OH)_2$) (Hansen et al. 2003; Doehne and Price 2010).

The cohesive effect of the silicate-based consolidants is due to the fact that they polymerise inside the stone, forming slowly silica gel. The reaction rate depends on weather conditions (humidity and temperature). Among these consolidants we must highlight tetraethylorthosilicate (TEOS) and ethyl silicate. These alkoxysilanes have a good durability and compatibility with stones and mortars with a high silicon content

(Franzoni, Pigino, and Pistolesi 2013). However, in carbonate stones, their effectiveness and durability is lower due to their low compatibility, as the union between carbonates and the silica gel is not strong, held together only by intermolecular forces (Sassoni et al. 2013). Furthermore, silica gel is prone to crack within the pores (Mosquera et al. 2008).

Among the polymeric consolidants, the main ones are epoxy and acrylic resins. Although epoxy resins have a great adhesive power, many restorers do not use them as consolidants because of their high viscosity, their fragility and their propensity to yellow during ageing (Doehne and Price 2010; Ginell and Coffman 2013; Krauklis and Echtermeyer 2018). On the other hand, the acrylic resins have been widely used in restoration processes. These thermoplastic copolymers derive from acrylics and methacrylates, have hydrophobic properties, and are chemically inert and stable under different environmental conditions (Vaz, Pires, and Carvalho 2008). However, their presence on the surface of the stone produces the occlusion of the porous system, the perspiration capacity of the stone decreases, yellowing occurs in the presence of UV radiation, etc. (Favaro et al. 2007; Vicini et al. 2001), so they are rather avoided unless it is strictly necessary.

Summarizing, despite the wide variety of biocides and consolidants, none of them fulfil all the requirements for their application in masonry of historic buildings, which makes compulsory the research for new products that could meet the demands without interfering in possible future treatments.

2. Nanotechnology. Basic considerations

Nanomaterials are materials of a size comprised between 1 and 1000 nm, although their size lies most commonly between 1 and 100 nm. This size provides the nanomaterial with new properties with respect to the macroscopic material (bulk), which are used by nanotechnology to achieve new applications (Cao 2004).

Among the multiple properties of nanomaterials, there is one that all of them share: the increase of specific surface against the macroscopic material. This property implies a greater interaction surface with the environment. The rest of the specific properties depend on their chemical composition and vary from the bulk properties.

There are several criteria for classifying nanomaterials. For example, based on composition, they can be classified as organic and inorganic nanomaterials (Sanjay and Pandey 2017).

The organic nanomaterials are formed by macromolecules based on carbon and they are subdivided into polymeric nanoparticles, dendrimers, liposomes and micelles (Heera and Shanmugam 2015), whereas inorganic nanomaterials, which are normally used in stone restoration, are classified in metallic nanoparticles, semiconductor nanoparticles or Quantum Dots, ceramic nanoparticles or metal oxides and carbon nanotubes (Khan, Saeed, and Khan 2017; Subbenaik 2016).

There are different methods to obtain these nanomaterials grouped into two categories: "Top-Down" and "Bottom-Up". The "Top-Down" methods consist in mechanically reducing macroscopic materials to a nanometric scale by grinding, abrasion or laser ablation processes. These are frequently-used processes in the synthesis of ceramic materials and metal oxides. The lack of uniformity of their size, as well as the difficulty of generating small nanomaterials (of only a few nanometres) are some of their disadvantages. On the other hand, “Bottom-Up” synthesis methods favour the aggregation of atomic or molecular precursors under optimized experimental conditions. This way, it is easier to regulate the shape and size of the nanomaterial, being sol-gel and chemical precipitation (Sepeur 2008; Karak 2019) the most common processes.

3. Nanomaterials in the conservation of stone masonries

The use of nanomaterials in the processes of conservation and maintenance of stone masonries may be considered one of the greatest contributions of nanotechnology in the last decades. The usage of the properties which materials achieve at a nanometric scale is allowing the development of different treatments adapted both to the substrate they are applied to and the function they must comply with. Accordingly, the use of metal nanoparticles and metal oxides, or the combination of some of them in the design of nanocomposites, have led to a new set of consolidating treatments, water repellents or biocides, some of which, after being tested in both laboratory and in buildings in situ have begun to be commercialized, for instance consolidating nanoparticles of $Ca(OH)_2$ (Nanoestore®, CaLoSil®) or SiO_2 (NanoEstel®) are already being used in restoration processes.

The interest to design and to assess the effectiveness of the treatments based on nanoparticles for the conservation of stone buildings has increased in the last 20 years. The diffusion of results in the field of architectural heritage has been numerically evaluated with a bibliographic research made in one of the most common search databases: Scopus (www.scopus.com). Figure 3 shows the tendency in the number of papers published by years that included the key words “nanoparticles” AND “stone” AND “Heritage”. The research results are 75 documents of which the 24% were published as open access. The first paper of the list (2001) is related to the consolidation with Ca(OH)2 nanoparticles (Ambrosi et al. 2001), one of the most studied treatments applied to the conservation of cultural heritage. Nevertheless, it was in 2013 when the number of researches increased remarkably with a trend that follows nowadays. The principal type of documents are articles (60), conference papers (7) and reviews (6), which were mainly published in journals (66), conference proceedings (6) and books

(3). Regarding the country of the research groups, Italy is the country that leads the investigations related to this item (49.3%), followed by Spain (21.3%) and Greece (10.6%).

3.1. Nanoparticles with biocide properties applicable in stone buildings

3.1.1. Titanium dioxide nanoparticles

Titanium dioxide nanoparticles (TiO_2) (Figure 4) have become one of the most versatile products for conservation-restoration treatments due to their chemical stability, their compatibility with traditional building products, their great photocatalytic activity, their applicability outdoors, etc. (Quagliarini, Bondioli, Goffredo, Licciulli, et al. 2012).

The current levels of environmental pollution generate multiple substances that are deposited or filter into the pores of the stones, which may cause aesthetic changes and degradation of the material by chemical reactions (Graziani et al. 2014). The use of TiO_2 nanoparticles help to generate a protective layer between the stony surface and the dirt deposits, which together with their photocatalytic and hydrophilic properties under ultraviolet radiation, keeps the stone unaltered as these deposits are easily removed or eliminated (Quagliarini, Bondioli, Goffredo, Cordoni, et al. 2012; Munafò, Goffredo, and Quagliarini 2015).

Some of the main advantages of TiO_2 nanoparticles are the chromatic inalterability of the surfaces after their application (Figure 3.C) (Quagliarini, Bondioli, Goffredo, Licciulli, et al. 2012) and their long-term stability as a photocatalytic treatment (Graziani et al. 2014; Munafò et al. 2014). Due to their versatility, these nanoparticles have also been studied as biocides (Munafò, Goffredo, and Quagliarini 2015; Goffredo et al. 2017), to remove and slow down the development of biofilms. Their biocidal action is based on their ability to promote the oxidation of the cell wall and to block the respiratory activity of microorganisms when irradiated with UV light (Foster et al. 2011). Some authors (Fonseca et al. 2010; Coutinho et al. 2016) have compared the efficacy of these nanoparticles with regard to commercial treatments based on quaternary ammonium salts, such as Biotin T® and Preventol RI80®. The results have proved the biocidal capacity of TiO_2 nanoparticles, which have a better long-term effect than both commercial treatments. However, the stone characteristics, i.e. porosity or roughness, can limit the efficiency of this nanoparticle as both self-cleaning and biocide treatment (Quagliarini et al. 2018).

3.1.2. Silver Nanoparticles

The use of silver as a disinfectant agent comes from ancient age, although its use began to decline with the introduction of antibiotics (Rai, Yadav, and Gade 2009). However, in recent decades, the development of this metal on a nanometric scale has resumed its use as a bactericide in the manufacture of everyday products such as clothing, masks, creams, textiles, cosmetics, food packaging and so forth, in disciplines as diverse as medicine, engineering or renewable energies (Gutarowska et al. 2012).

The bactericidal mechanism of action of the silver nanoparticle has not been completely elucidated, although there is evidence that it is a multifactorial process which causes damage to both the cell wall and the plasma membrane of the bacteria, and it also inhibits DNA replication and protein synthesis(Lok et al. 2007). This effect is mainly because silver nanoparticles release steadily Ag^+ ions from their surface, which favours their biocidal effect in concentrations lower than those in silver salts such as silver nitrate ($AgNO_3$). This effect has been found in many microorganisms (Gram-positive and Gram-negative bacteria, microalgae, fungi…) (Lok et al. 2007; Banach and Pulit-Prociak 2016; Nowicka-Krawczyk, Zelazna-Wieczorek, and Koźlecki 2017), and their biocidal activity has been associated with nanoparticle size (Lok et al. 2007), shape

(Pal, Tak, and Song 2007) and the reduction agent used in its synthesis (Van Dong et al. 2012) (Figure 5).

The main advantages of silver nanoparticles compared with other traditional biocides are that they are long-term stable bactericidal agents with long-lasting effect, effective on a wide variety of microorganisms in which resistance is unlikely to be generated, with low toxicity for humans and the environment (Rai, Yadav, and Gade 2009; Essa and Khallaf 2014).

Studies on the application of silver nanoparticles to inhibit biodeterioration in construction materials are numerous (Eyssautier-Chuine et al. 2015; Carrillo-González et al. 2015; Essa and Khallaf 2014), and they have proved to have a greater inhibitory effect than some traditional biocides, as for instance Biotin T® (Javier Becerra, Mateo, et al. 2019). Sometimes, these nanoparticles are used together with other consolidating products as, for instance, its application together with acrylic or silicic polymers in the tests carried out on stone samples from the Temple of Edfu and the tomb of Teti-ankh-km in the Sakkara region (Nuhoglu et al. 2006). In other cases, the use of an alkoxylan has not acted as a hardener for the stone, but has improved the adhesion of the nanoparticle to the stone substrate without modifying its shape or size(Bellissima et al. 2014).

One of the main disadvantages is the silver's capacity of staining (Ruffolo et al. 2017; Graziani, Quagliarini, and D'Orazio 2016) (Figure 5.C), this is the reason why it must be used at low concentrations. Their use at low concentrations makes it difficult to detect their penetration profiles in the stone as the limit of detection of the SEM-EDX technique, usually used in diagnosis, is above 1,000 ppm (Kearton and Mattley 2008) and this is higher than that of the concentrations generally used in the treatment, so they cannot be detected. Recent research of our group has provided a solution through the use of more sensitive techniques such as Laser-induced breakdown spectroscopy (LIBS) (Mateo et al. 2019; Javier Becerra, Mateo, et al. 2019), which allows detecting the nanoparticle and generating penetration profiles.

3.1.3. Zinc oxide nanoparticles

ZnO nanoparticles can act as biocides due to their capacity to generate reactive oxygen species that break the cell wall, both in microorganisms and in spores (V. V. Kumar and Anthony 2016). This property depends on the nanoparticle shape and size, increasing its biocidal effect as the size decreases (Cepin et al. 2015). These nanoparticles have been studied as biocides in the context of the conservation of historical heritage. Their main advantage is that they produce little colour change on pale substrate, unlike other bactericidal nanoparticles such as copper oxide ones (Van der Werf et al. 2015), with a similar capability to inhibit the biofouling growth that the silver nanoparticles (Javier Becerra, Ortiz, Zaderenko, et al. 2019). Additionally, they have a lower cost in relation to other types of metal nanoparticles (Noeiaghaei, Dhami, and Mukherjee 2017), and their biocidal capacity has also been proved in other construction materials such as wall paintings (Gambino et al. 2017)and wood (Huang, Lin, and Hsu 2015).

3.1.4. Copper oxide nanoparticles

Copper oxide nanoparticles (CuO) is another low cost alternative to traditional biocides and have been shown to have greater stability than other metal nanoparticles such as Cu^0 or Ag^0 nanoparticles, which are sensitive to oxygen and light (Zarzuela et al. 2018).

The biocidal effect of these nanoparticles is due to different mechanisms related to the release of Cu^{2+} ions, causing oxidative stress, damage to the cell membrane and DNA fragmentation in different microorganisms (V. V. Kumar and Anthony 2016). It has also been found that they interfere in photosynthetic processes by means of indirect mechanisms such as oxidative stress or the reduction of cellular exchange with the environment (Perreault, Samadani, and Dewez 2014). However, despite their biocidal properties (Kruk et al. 2015; Zarzuela et al. 2017), CuO nanoparticles have been less studied for their use in stone restoration than other types like silver or TiO_2 ones. Among the first investigations, Zarzuela et al. (Zarzuela et al. 2018; Zarzuela et al. 2017)evaluated their biocidal effect together with SiO_2 consolidant nanoparticles. Their results confirmed the capacity of these nanoparticles to reduce the growth of microorganisms. The inhibiting effect of TiO_2/CuO nanocomposites has also been studied, although its inhibiting activity was lower than those achieved by Ag/TiO_2 nanocomposites (Graziani, Quagliarini, and D'Orazio 2016).

3.1.5. Silver/titanium dioxide nanocomposite

A nanocomposite can be defined as a nanomaterials that combine different components in order to improve the properties of each component (Okpala 2013). In this sense, different nanocomposites have been researched as biocide treatments for stone heritage, i.e., TiO_2/CuO (Graziani, Quagliarini, and D'Orazio 2016), TEOS/Ag (Jalali and Allafchian 2016),… Nevertheless, the nanocomposite more studied for the protection of stone materials is Ag/TiO_2 nanocomposites. In this nanocomposite, the properties of each nanoparticles are improved with respect its use separately. Among the improved properties, it is worth highlighting that the TiO_2 nanoparticle is not only reactive in UV, but also in the visible spectrum. This is due to the presence of silver ions, which increases the electronic mobility of TiO_2. As a consequence, the catalytic activity of TiO_2 does not depend only on the small UV component of the solar radiation spectrum (3-5%), eliminating one of the greatest limitations of the nanoparticles when used in isolation (Zhao et al. 2012).

As a general rule, this type of nanocomposite consists of a core of TiO_2 on which the silver nanoparticle is deposited (Figure 6). Its biocidal effect has been proved in several microorganisms (bacteria, fungi, …) (Yaşa et al. 2012; Lungu et al. 2014), just like the nanocomposite with reverse structure (Lin et al. 2011).

The synergistic effect generated between both nanoparticles has been confirmed by Becerra et al.(J. Becerra et al. 2018) when the Ag/TiO_2 nanocomposite improved the biocidal properties of both of them separately. Within the field of conservation-restoration of stone elements, the first studies have confirmed the biocidal properties of this nanocomposite, both in liquid culture (Javier Becerra, Zaderenko, and Ortiz 2017)and agar plates (La Russa et al. 2014). Other studies have focused on the analysis of their antibacterial properties (Bellissima et al. 2014; Aflori et al. 2013), including the inhibition of biofilms in a marine environment (Ruffolo et al. 2013; Ruffolo et al. 2017), or the comparison of their capacity to inhibit biofilms of microalgae compared to TiO_2 nanoparticles(Goffredo et al. 2017). It has also been proved that the adhesion of these treatments to the stone surface is related to the roughness and porosity of the substrate, in such a way that in low porosity stones adhesion decreases causing a greater aesthetic impact (Lettieri et al. 2017; Graziani, Quagliarini, and D’Orazio 2016).

3.2. Nanoparticles with consolidating properties in stone materials

3.2.1. Calcium hydroxide nanoparticles

One of the greatest exponents of nanotechnological development in conservation and restoration is the use of $Ca(OH)_2$ nanoparticles as a consolidating treatment for stone materials and mortars (Figure 7). In addition to the advantages of the use of lime as a consolidant, as previously stated, we must add others due to the size of the $Ca(OH)_2$ nanoparticles (50 to 600 nm), such as the improvement in the penetration of the treatment (Chelazzi et al. 2013), the increase of reactivity and of the applied concentration of $Ca(OH)_2$ (Giovanni Borsoi et al. 2018). Furthermore, these nanoparticles can be applied as suspensions in short chain alcohols, such as 1-propanol, which eliminates the risks associated with the use of water (dissolving or recrystallizing substances, and so forth) (Baglioni et al. 2014).

Nowadays, and despite their commercialization (Nanorestore® or CaLoSil®), $Ca(OH)_2$ nanoparticles are still being studied in order to check and improve their consolidating properties (Rodriguez-Navarro, Suzuki, and Ruiz-Agudo 2013). Thus, not only the optimal way of obtaining the nanoparticle (Chelazzi et al. 2013; Daniele, Taglieri, and Quaresima 2008) or the concentrations and means of application (Rodriguez-Navarro, Suzuki, and Ruiz-Agudo 2013) is analysed, but also the suitability of its use together with other nanoparticles such as barium or magnesium hydroxide (Chelazzi et al. 2013).

Despite their use in numerous tests on masonries (Gomez-Vilalba et al. 2011; Baglioni et al. 2014) and the good results achieved as pre-consolidating material (Rodriguez-Navarro, Suzuki, and Ruiz-Agudo 2013; G. Borsoi et al. 2015), their effectiveness is reduced when in-depth consolidation is required (Giovanni Borsoi et al. 2017). This is due to the migration of the nanoparticles back to the surface of the treated material during the solvent evaporation process (G. Borsoi et al. 2015; Giovanni Borsoi et al. 2016; Costa and Rodrigues 2013; Taglieri et al. 2018), which can sometimes cause the appearance of whitish veils on the surface (van Hees, Veiga, and Slížková 2017; Jang and Matero 2018). To improve penetration, studies have focused on the use of several solvents. Short-chain alcohols have achieved the best results (Poggi et al. 2016; Rodriguez-Navarro, Vettori, and Ruiz-Agudo 2016). However, in order to favour the in-depth consolidation, it is necessary to take into account the texture, roughness, porosity and porometry of the stone, together with the kinetic stability of the applied nanoparticle solution (Giovanni Borsoi et al. 2017). To determine the in-depth penetration of $Ca(OH)_2$ nanoparticles in stone substrates, they have been doped with quantum dots of ZnO during the synthesis process (Javier Becerra, Ortiz, Martín, et al. 2019), which can be tracked by fluorescence (Figure 8). This nanocomposite also allows to discern easily between treated and not treated areas, while the methods based on imagen analysis and segmentation require a high contrast between consolidating aggregates and stone to achieve a clear separation between the background and the coating (Lanzón et al. 2019).

3.2.2 Silicon oxide nanoparticles

Silicon-based nanocomposites have been widely studied and used as stone consolidants. The use of silicon oxide nanoparticles (SiO_2) reduces the reaction time for silica gel formation and avoids the use of toxic solvents (Gheno et al. 2018).

Among the main disadvantages of these nanoparticles we could point out the capillary stresses generated in the drying stage, which can cause cracks inside the stone (Luo, Xiao, and Zhang 2015). To reduce the stresses generated during the polymerization process, the use of surfactants, such as n-octaline, has been proposed (De Rosario et al. 2015; Mosquera et al. 2008). Their poor penetration (Figure 9) when the silica gel develops on the surface of the stone (Falchi, Balliana, and Izzo 2013), and their bad weathering in accelerated weathering assays by salt crystallization (Vasanelli et al. 2019), are others of their main disadvantages. This effect has been minimized by applying the treatment in environments with high relative humidity (Zornoza-Indart and Lopez-Arce 2016).

An additional application of silicon nanomaterials which is being actively researched is the development of water-repellent surfaces. Thus, the use of SiO_2, and its derivatives with different organic groups, increases the water repellence on the surface (De Ferri et al. 2011). An example of this development is the commercial product Tecnadis PRS®, which has been tested in the Cathedral of Santiago de Compostela (Spain) (ArteLab S.L. 2013). SiO_2 nanoparticles have also been tested together with TiO_2 nanoparticles to generate self-cleaning surfaces in stone walls (Kapridaki et al. 2014; Pinho et al. 2013), when the hydrophobic properties of the SiO_2 nanoparticles and the catalytic properties of the TiO_2 nanoparticles act together.

4. Conclusions

Currently, there is an acceleration in degradation processes of masonry as a consequence of climate change and increasing environmental pollution. The treatments that have been traditionally used in conservation and restoration processes have important drawbacks such as low effectiveness, incompatibility with the original material, bad ageing, etc., and do not fulfil the requirements for use in historical heritage. An approach based on nanotechnology tries to cater for this need by designing specific treatments based on the special properties of nanomaterials. Among the treatments that incorporate nanotechnology, consolidants and biocides stand out. Consolidant treatments based on inorganic compounds, with a similar composition to stone, are expected to have a high long-term chemical compatibility. Nonetheless, sometimes they form whitish veils or shallow layers, as in the case of $Ca(OH)_2$ and SiO_2 nanoparticles, respectively, which might be unacceptable on aesthetic grounds. The application method, the solvent and the concentration of nanoparticles used can reduce these disadvantages, without compromising their effectiveness.

When dealing with biocidal treatments based on nanoparticles, the existence of a wide range of nanomaterials allows one to choose the most suitable one according to the properties of the masonry to work on. To this effect, it is important to bear in mind that certain nanoparticles tend to generate slight increases in colour, such as silver and copper-based nanoparticles, so the concentrations applied must guarantee that changes remain within the accepted range for historical heritage.

Despite the fact that some of those treatments are already available commercially, medium and long-term studies are still running on.

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Table 1.Summary of the main alterations caused by microorganisms on stone (adapted from Gaylarde et al. [8]).

Microorganism	Black crust	Coloured patches	Crack	Crust	Decolouratio-	Detachment	Exfoliation	Patina	Pitting	Powdering
Autotrophic bacteria	X						X	X		X
Heterotrophic bacteria	X						X	X		
Cyanobacteria								X		
Algae								X		
Fungi		X					X		X	
Lichens		X		X					X	
Mosses and liverworts		X			X					
Higher plants			X			X				

Table 2. Main indicators of alteration in stone associated to loss of cohesion and material.

Type of decay	Level of damage (Low ⟶ High)		
Fissure	Crack	Fracture	Fragmentation
Decohesion	Erosion	Powdering/sanding	
Loss of materials			
Formation of cavities	Pitting	Alveolization	Coving
Scaling/delamination	Scaling	Exfoliation	Delamination
Irregular	Loss of material		

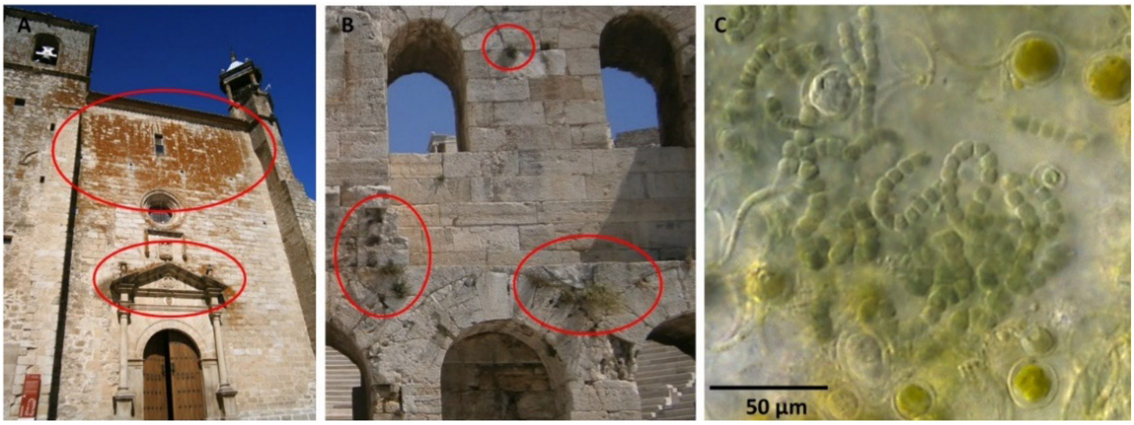
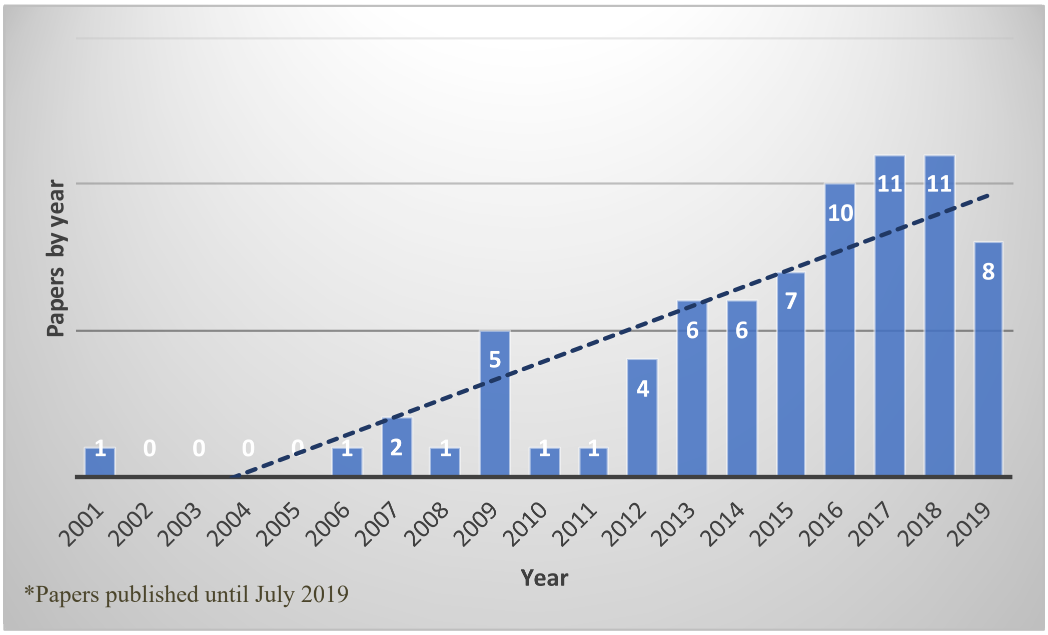


Figure 1.

Figure 2.



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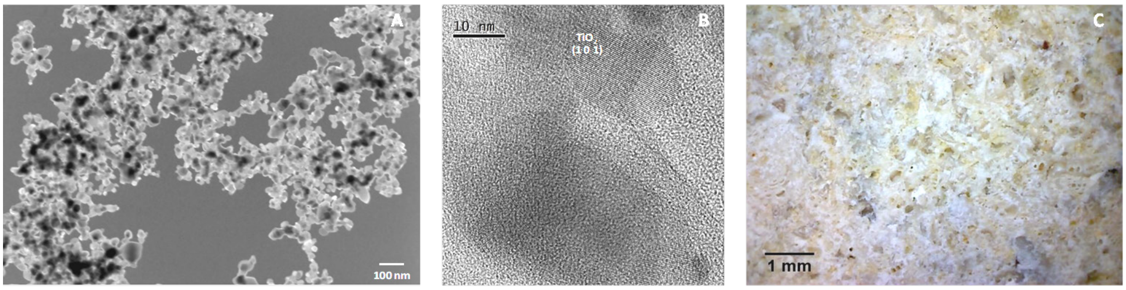

Figure 4.

A

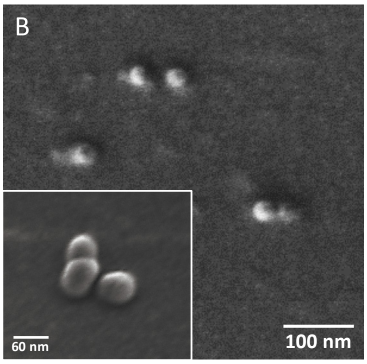

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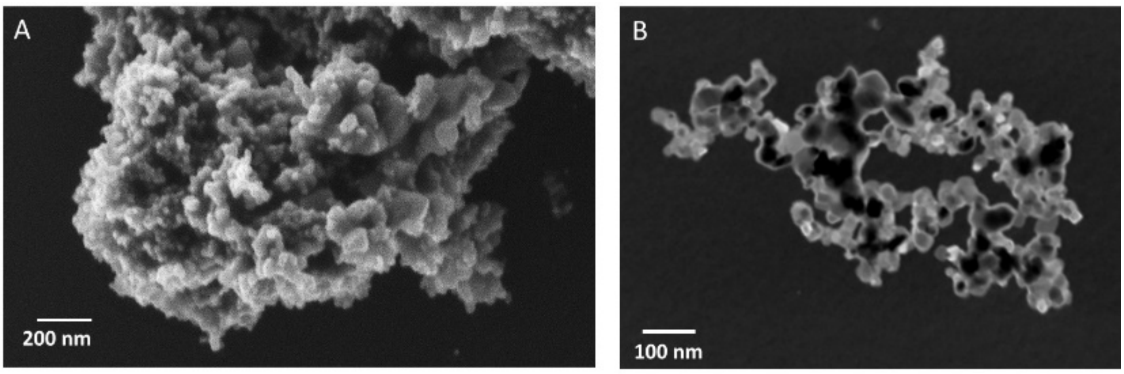
Figure 5.



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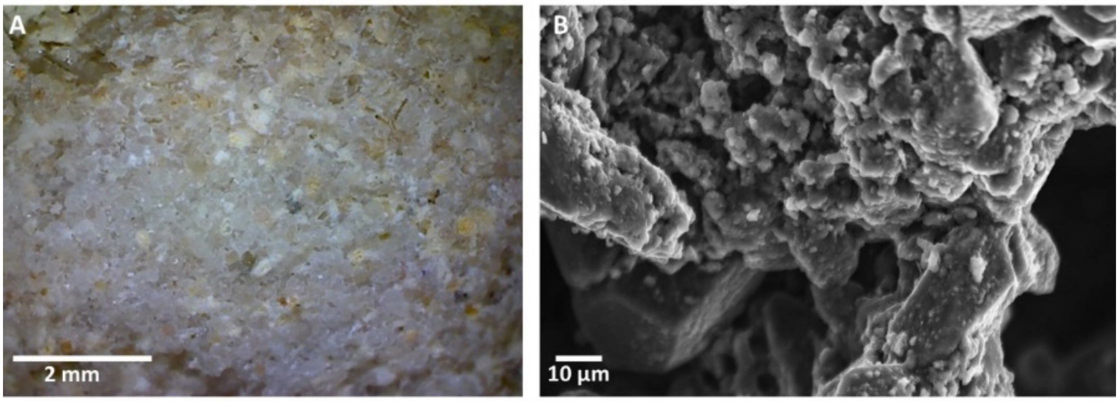

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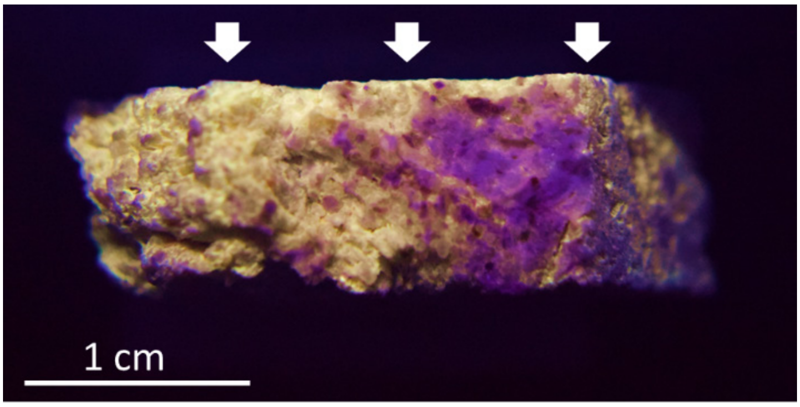

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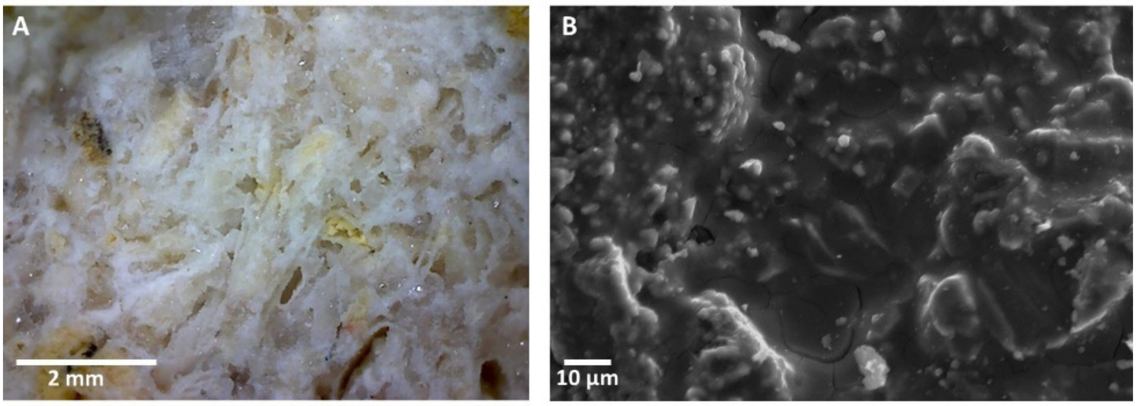

Figure 9.

Figure captions

Figure 1. Biodeterioration on (A) the main facade of San Martin’s Church (Trujillo, Spain) and (B) upper floors in the back of the front of the stage in Dionisio Theatre (Athens, Greece). The most affected areas have been marked in red in the pictures. (C) Microscope image of microorganisms present in a biofilm from the facade of Santa Cruz Church (Seville, Spain), in which species of the genus *Monoraphidium*, mainly *Nostoc* and *Chlorella* are seen.

Figure 2. (A) Erosion in the reliefs of the Arch of Galerius (Thessaloniki, Greece). (B) Detail of black crust in Charles' Bridge (Prague, Czech Republic). (C) Alveolization in the wall of Panama City (Panama).

Figure 3. Diffusion over the time of the papers whose issue is related with the application of nanoparticles in stones.

Figure 4. (A) SEM picture of commercial product P25 (Degussa®) in which TiO_2 nanoparticles can be observed in the two crystalline phases that compose it, rutile and anatase. (B) TEM picture of the same nanoparticles, in which the periodicity of their crystalline planes is visible. (C) Limestone treated with TiO_2 nanoparticles.

Figure 5. (A) Inhibition halo caused by the presence of silver nanoparticles on a bacterial lawn of Gram-negative *Escherichia coli* bacteria on an agar plate. (B) SEM image of spherical silver nanoparticles synthesized using sodium borohydride as a reducing agent and sodium citrate as a stabilizing agent. (C) Limestone slabs treated and untreated (inset) with silver nanoparticles.

Figure 6. Ag/TiO_2 nanocomposite. (A) SEM image of the topography of a nanocomposite aggregate. (B) Dark field STEM image showing the arrangement of Ag nanoparticles on the surface of the TiO_2 nanoparticle (white spots).

Figure 7. (A) Image of the surface of a limestone treated with $Ca(OH)_2$ nanoparticles. (B) SEM image of the same limestone in which we can appreciate the $CaCO_3$ aggregates consolidating the stone matrix.

Figure 8. Limestone treated with $Ca(OH)_2$ nanoparticles doped with ZnO quantum dots. The yellow fluorescence of the quantum dots enables the determination of the penetration depth of the treatment. The white arrows point to the face on which the treatment was applied.

Figure 9. (A) Image of the surface of a limestone treated with SiO_2 nanoparticles. (B) SEM image of the same limestone where we can observe the formation of a silica gel film on the surface, as well as cracks formed due to the stresses generated during the polymerization.